Tripodal Triamidometallates of the Heavy Group 14 Elements: Inorganic Cages with Remarkable "Ligand Properties"

Lutz H. Gade[a]

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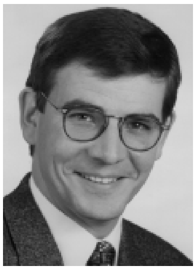
Anionic main group metal donors with potentially interesting ligand properties are obtained if ate complexes of the heavy p-block metals are formed by coordination between tripodal amides and divalent group 14 metal centres. The limitations of this approach, due to the potential oxidation by the central transition metal atom, may in part be suppressed by the presence of electronegative substituents at the M^{II} centre, which makes the metallates less reducing. The considerable stability of the triamidostannates(II) towards Ag^{I} or Au^{I-III} is testimony to the practical significance of this. The most characteristic structural consequence of the rigid amido cages is the well-defined orientation of the peripheral N-substituents, which gives rise to very large cone angles for the monodentate ligands in their transition metal complex derivatives. These angles considerably exceed those of "ordinary" metallate groups or of the isolobal neutral group 15 ligands, and so would be expected to favour low coordination numbers in transition metal complexes.

Introduction

Molecular cages made up of main group metals, and also non-metals, have emerged as a basic structural principle in inorganic chemistry. They range from aggregates representing simple geometric bodies, such as the ubiquitous $\{M_4X_4\}$ cubes,[1] to very large, multi-shell "cluster" structures.[2]

Molecular fragments containing nitrogen and oxygen atoms, the components of amide, imide and alkoxide cages, have been studied in great detail. The field was comprehensively reviewed by Veith a decade ago,[3] and has reappeared in several more specialized overviews since.[4] In recent years, mixed-metal cage structures have attracted increased attention. Their rational synthesis (or at least an a posteriori rationalization of their assembly) remains a challenge and a current focus of research. In a perceptive analysis of the results of their work in this field, Wright et al. suggested that the p-block metals play the dominating role in dictating the structures of the mixed s-/p-block cage compounds.[5] This is thought to be the case since greater metal−ligand covalency of the metal−ligand interaction, and thus greater directionality of the bonding, results in more rigid metal coordination.

Several years ago, Veith and co-workers demonstrated that mixed metal alkoxide cages may be employed as (neutral) ligands in transition metal complexes.[6] Anionic main group metal donors with potentially interesting ligand properties are obtained if ate complexes of the heavy p-block metals are incorporated into such an array without "intra-cage" charge compensation. A conceptually simple



Lutz H. Gade is a full professor of chemistry at the Université Louis Pasteur, Strasbourg and the Head of the Laboratory of Organometallic Chemistry and Catalysis. After completing his undergraduate studies at the University of Bonn and the Technical University of Munich, he went to Cambridge to work for his Ph.D. with Jack Lewis. Having returned to Germany after completing his thesis in 1991, he joined the Chemistry Department at the University of Würzburg, where he finished his habilitation in 1996 and where he subsequently worked as a lecturer. In 1998 he moved to Strasbourg to take up his present position, and in summer 2000 he was elected a member of the Institut Universitaire de France. His research interests are in the fields of coordination chemistry, organometallic chemistry and catalysis.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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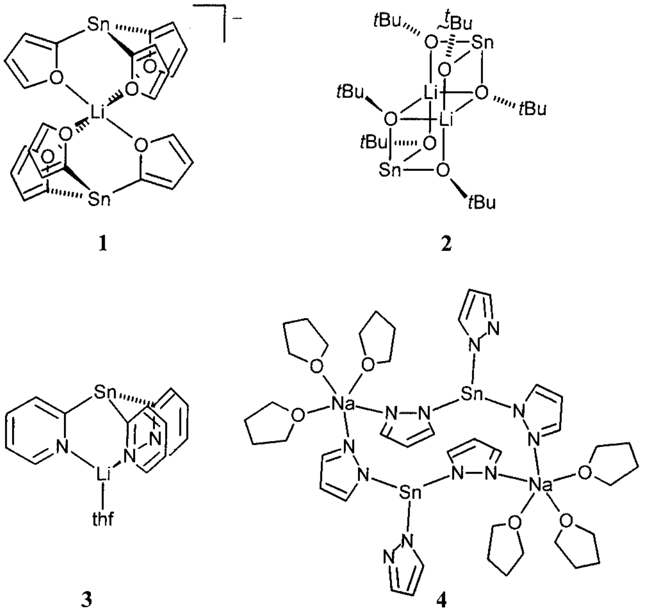
[a] Laboratoire de Chimie Organométallique et de Catalyse (CNRS UMR 7513), Institut Le Bel, Université Louis Pasteur Strasbourg,
4, rue Blaise Pascal, 67070 Strasbourg, France

approach that employs this strategy is based on a polydentate ligand with podand topology coordinating to a low-valent p-block metal and thus forming the anionic keystone of a ligand cage. The tripodal amides, which we introduced to the coordination chemistry of the early transition metals in the early 1990s,[7] have proved to be ideally suited for the pursuit of this goal and offer straightforward means of ligand design based on the metal cages. The recent progress in this field is the topic of this overview.

Metallates of the Divalent Group 14 Metals

The structural chemistry of anionic trisubstituted metallate(II) compounds of group 14 elements has received considerable attention. It began to develop in the 1980s, thanks to significant improvements in crystal preparation techniques and low-temperature crystal data collection. Veith and co-workers characterized a whole series of lithium trialkoxygermanates(II), -stannates(II) and -plumbates(II) that displayed characteristic cage structures, such as [Li(μ-$C_4H_3O)_3Sn$] (**1**) and [{Sn(O*t*Bu)$_3$M}$_2$] (**2**), shown in Figure 1.[8]

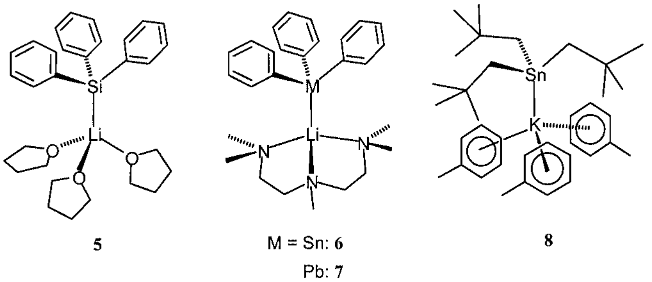


1 **2** **3** **4**

Figure 1. Four representative examples of cation−anion aggregation in stannates(II)

More recently, Wright et al. reported the structure of [Pb(2-py)$_3$Li(THF)] (**3**),[9] and Stalke and co-workers published the synthesis and X-ray diffraction study of several tris(pyrazolyl)germanates(II) and -stannates(II), such as [{(Pz)$_3$SnNa(THF)$_3$(PzH)}$_2$] (**4**), in which the heteroatom donor ligands at the p-block atom also serve as bridging units between the cations and metallate anions.[10]

A particularly interesting class of alkali metal group 14 and group 15 metallates are those containing a direct metal−metal contact between the cationic and the anionic metal centres, as found in the crystal structures of [$Ph_3Si-Li(THF)_3$] (**5**),[11] [Ph_3Sn-Li(pmdeta)] (**6**)[12] and [Ph_3Pb-Li(pmdeta)] (**7**)[13] (Figure 2).



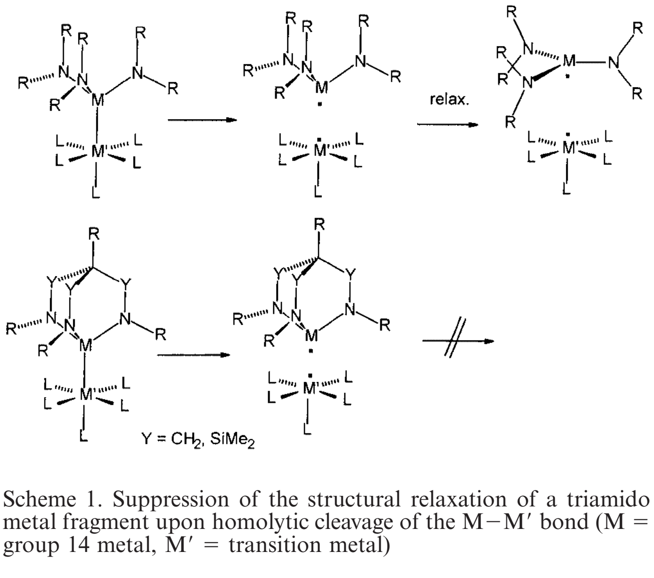
5 M = Sn: **6** Pb: **7** **8**

Figure 2. Metal−metal bonds between alkali metals and group 14 metals in trialkyl/aryl metallates(II)

The presence of a direct K−Sn bond was established both by NMR spectroscopy (^{119}Sn-^{39}K coupling) and by X-ray diffraction for the complex [$(Me_3CCH_2)_3Sn-K(toluene)_3$] (**8**), isolated by Lappert and co-workers from the reaction between the distannane [$(Me_3CCH_2)_3Sn]_2$ and potassium metal.[14] The systematic synthesis and structural investigation of these heterodimetallic compounds has also been extended to the heavier group 15 elements.[15]

The Tripodal Triamido Metallate Cages as *Ligands*: Some Basic Conceptual Considerations

An important consequence of the integration of divalent group 14 metal centres into the rigid cage structures of the tripodal triamidometallates is the reinforced pyramidality of the M^{II} centre. Thus, structural relaxation and concomitant stabilization of the $M(NR_2)_3$ fragment upon homolytic cleavage of M−M′ (M′ = transition metal) bonds in derivatives of these compounds is inhibited (Scheme 1). As for the stabilization of the triamido transition metal fragment in the early−late heterodimetallic complexes previously studied by us, destabilization of the amido complex fragment therefore contributes to the thermodynamic stability

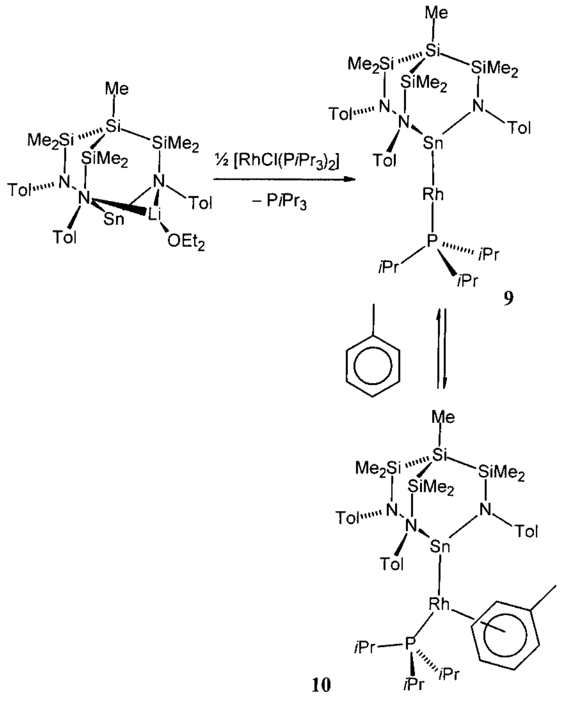


Scheme 1. Suppression of the structural relaxation of a triamido metal fragment upon homolytic cleavage of the M−M′ bond (M = group 14 metal, M′ = transition metal)

of the M−M′ complexes (or, viewed alternatively, to the stability of the complexation of M′ by the triamidometallate).[16]

The use of a divalent group 14 metallate as a ligand may in principle be limited by potential oxidation by the central transition metal atom. This may in part be suppressed by the presence of electronegative substituents at the M^{II} centre, which makes the metallates less reducing. Electronegative amido nitrogen atoms at the metal centre are therefore well suited for this purpose, and would be expected to match the established robustness of the halides and alkoxides. The considerable stability, discussed below, of the triamidostannates(II) studied in our group towards Ag^{I} or Au^{I-III} is testimony to the practical significance of this consideration.

The most characteristic structural consequence of the rigid amido cages is the well-defined orientation of the peripheral N-substituents, which gives rise to very large cone angles for the monodentate ligands in their transition metal complex derivatives. These angles considerably exceed those of "ordinary" metallate groups or of the isolobal neutral group 15 ligands, and thus should be expected to favour low coordination numbers in transition metal complexes. An illustrative example is the reaction product of $[Me\{SiMe_2N(p\text{Tol})\}_3SnLi(THF)_3]$ and the rhodium complex $[Rh_2Cl_2(Pi\text{Pr}_3)_4]$ (Scheme 2).[17]



Scheme 2. Synthesis of the Sn−Rh complex **10**, which is in equilibrium in solution with the 12-electron complex **9**

A low-temperature ^{31}P, ^{13}C and ^{1}H NMR study in [D8]toluene indicated the existence of a free 12-electron dicoordinate species **9**, which appeared to be in rapid equilibrium with the 18-electron complex **10** bearing an η^6-toluene ligand. The molecular structure of the isolated, crystalline solid **10** was determined by an X-ray diffraction study (Figure 3).[17]

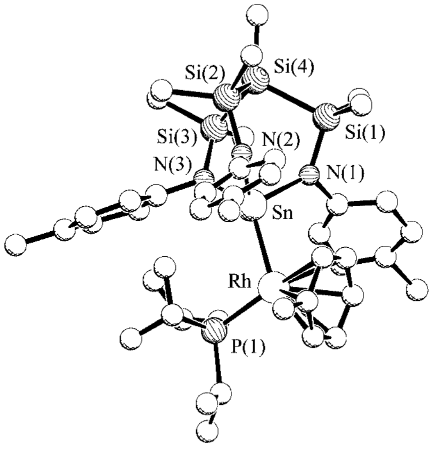


Figure 3. Molecular structure of $[Me\{SiMe_2N(p\text{Tol})\}_3Sn-Rh(Pi\text{Pr}_3)(\eta^6\text{-toluene})]$ (**10**)

The Structural Diversity of Lithium Triamidometallates Containing Tripodal Amido Ligands

As discussed above in more general terms, an interesting aspect of the structural chemistry of the lithium triamidometallates in solution and in the solid state is the type of interaction between the anionic cage and the counter-cation (in most cases solvated Li^+). Both solvent-separated salts and contact ions have been found. In the latter, the alkali metal ion is either directly bound to the group 14 metal (**I**) (Figure 4), in what is thought to be a primarily ionic metal−metal bonding interaction, or attached to the amido nitrogen atoms in a bridging coordination mode (**II**), thus breaking the overall threefold symmetry of the system.

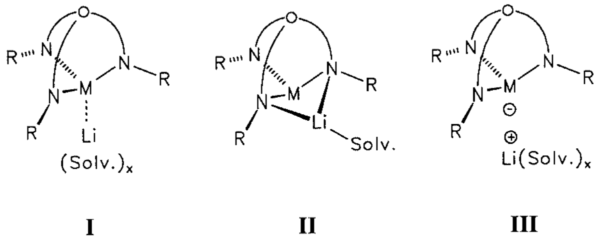


Figure 4. Three types of anion−cation association in lithium triamidometallates(II) of the group 14 elements

Treatment of the isolated lithium amides $[HC\{SiMe_2N(Li)(p\text{Tol})\}_3]$ and $[HC\{SiMe_2N(Li)[(S)\text{-1-(1-naphthyl)ethyl}]\}_3]$ with 1 mol-equiv. of $SnCl_2$ at 0 °C in diethyl ether/THF gave the lithium triamidostannates $[HC\{SiMe_2N(p\text{Tol})\}_3Sn-Li(THF)_3]$ (**11**)[18] and $[HC\{SiMe_2N[(S)\text{-1-(1-naphthyl)ethyl}]\}_3Sn-Li(THF)_3]$ (**12**), respectively.[12] Both compounds were characterized by single-crystal X-ray structure analyses and found to possess direct Sn−Li bonds (**11**: 2.93 Å; **12**: 3.06 Å) (Figure 5).

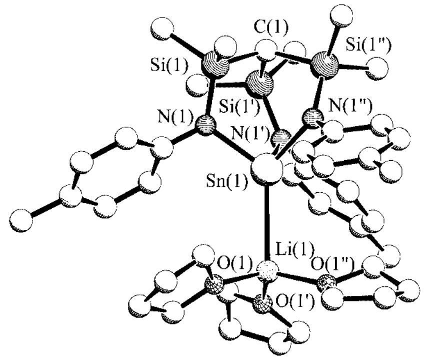


Figure 5. Molecular structure of [HC{SiMe$_2$N(pTol)}$_3$-SnLi(THF)$_3$] (**11**)

In the molecular structure of **11**, the Sn atom is displaced by 1.16(1) Å from the plane defined by the three amido nitrogen atoms, which have trigonal-planar geometry [$\Sigma\{<_N\}$ = 359.9(8)°].[18] The average <(N−Sn−N′) of 93.3(4)° in the trigonal-monopyramidal SnN_3 unit indicates that Sn−N σ-bonding primarily involves the 4p orbitals of the tin atom, with the lone pair residing in a molecular orbital of essentially 4s character. However, it should be pointed out that the partially ionic nature of the Sn−N bonds may render orbital overlap and hybridization less important than in alkyl or aryl stannates. The absence of ionic conductivity of solutions of **11** in THF or diethyl ether indicates that the situation of a contact ion pair pertains even in a polar environment.

In view of the structure determined for **11**, it was of interest whether the presence of an additional stronger donor ligand would effect the disruption of the Sn−Li contact and produce an ion pair. The synthesis of compound **11** from the lithium amide and $SnCl_2$ in the presence of 2 mol-equiv. of pentamethyldiethylenetriamine (pmdeta) gave an anion−cation complex that was formulated as [{MeN-($CH_2CH_2NMe_2$)$_2$Li}$_2$Cl][HC{SiMe$_2$N(4-$CH_3C_6H_4$)}$_3$Sn] (**13**).[18,20] A single-crystal X-ray structure analysis of **13** revealed that the Li^+ counterion is indeed separated from the stannate anion [HC(SiMe$_2$NpTol)$_3$Sn]$^-$ through coordination by a pmdeta ligand and a ClLi(pmdeta) unit to generate the complex cation [{MeN($CH_2CH_2NMe_2$)$_2$Li}$_2$Cl]$^+$ (Figure 6).

In the crystal, the cation rides in a "piggyback" fashion on the trisilylmethane side of the stannate anion, and there is no significant interaction with the tin atom.[20]

A molecular structure in which a contact ion pair adopts a type **II** arrangement, with the lithium ions attached to the amido nitrogen atoms in a bridging coordination mode, was found in the triamidoplumbate [MeSi{SiMe$_2$N(tBu)}$_3$-PbLi(THF)] (**14**).[18] In general, triamidoplumbates containing tripod-amido ligands were most conveniently synthesized by treatment of the lithium amides with plumbocene, which avoided the competing redox reactions found with use of $PbCl_2$ (Scheme 3).[21] An X-ray diffraction study of **14** revealed that the (tripod-amido)plumbate cage comprising the four silicon atoms of the trisilylsilane unit and the PbN_3 unit is significantly distorted, due to the coordination of the (THF)Li^+ "counterion" to two of the amido nitrogen atoms (Figure 7).

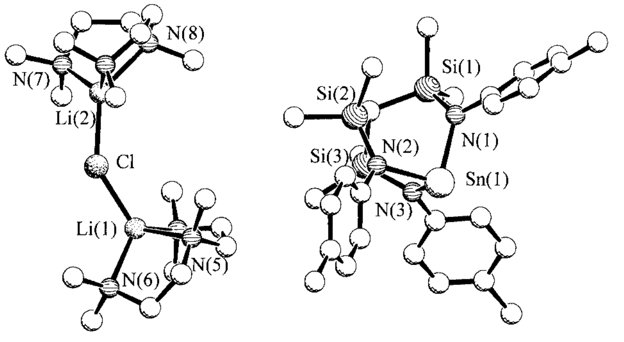
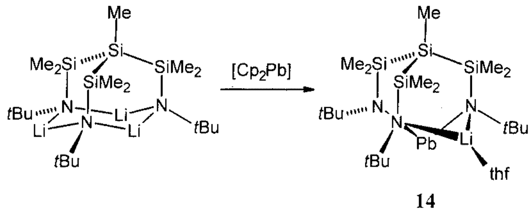


Figure 6. Representation of the molecular structure of [{MeN($CH_2CH_2NMe_2$)$_2$Li}$_2$Cl] [HC{SiMe$_2$N(4-$CH_3C_6H_4$)}$_3$Sn] (**13**), showing the relative cation−anion arrangement in the crystal



Scheme 3. Synthesis of the triamidoplumbate **14** by treatment of the lithium amide with plumbocene

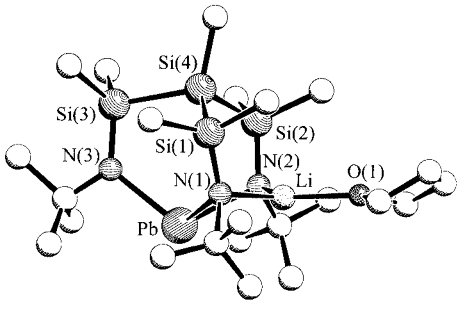
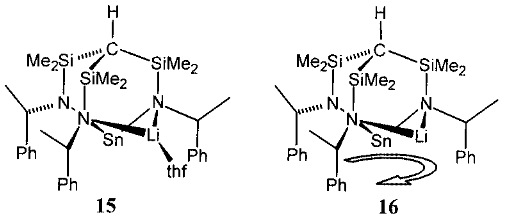


Figure 7. Molecular structure of the lithium triamidoplumbate [MeSi{SiMe$_2$N(tBu)}$_3$PbLi(THF)] (**14**)

The molecule has idealized C_s symmetry, the virtual mirror plane being spanned by Si(4), Si(3), N(3), Pb(1), Li(1) and O(1). As a consequence of the binding of the (THF)Li group to the amido framework, the geometry of the two N-functions involved deviates from the trigonal planarity observed for the N(3) atom [$\Sigma\{<_{N(1)}\}$ = 346(2)°, $\Sigma\{<_{N(2)}\}$ = 350(3)°; however, $\Sigma\{<_{N(3)}\}$ = 359(3)°]. Moreover, steric repulsion between the THF ligand and the N(1)- and N(2)-bonded tBu groups forces the latter apart. On the other hand, the Li atom "ties" the two amido nitrogen atoms together to generate an N-donor atom arrangement that deviates from the otherwise more or less undistorted trigonal-monopyramidal arrangement of the N_3Pb unit

[<N(1)−Pb(1)−N(2) = 82.5(9)°, but <N(1)−Pb(1)−N(3) = 103(1)° and <N(2)−Pb(1)−N(3) = 109(1)°].

In the structure of **14**, the THF molecule coordinated to Li^+ is located between two of the peripheral N-substituents. This arrangement blocks potential cation mobility, which appears to require the absence of Li-bound co-ligands. We have been able to synthesize both the solvated (**15**) and the THF-free (**16**) lithium stannates of the C_3-chiral triamido cage $[HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3Sn]^-$ (Scheme 4), of which **15** was characterized by X-ray crystallography.[22]



15 **16**

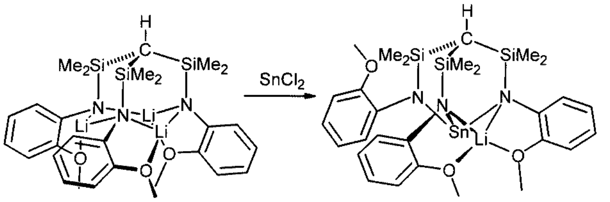
static dynamic

Scheme 4. "Locking" the cation mobility in a lithium triamidostannate by coordination of a co-ligand (THF)

While the signal patterns in the NMR spectra of **15** and **16** indicate closely related structures and are consistent with a retention in solution of the structural arrangement established for crystalline **15**, both compounds differ significantly with respect to dynamic behaviour in solution.[22] The coordinated THF ligand appears to "lock" the Li cation in the position between the two N atoms, thus conferring structural rigidity upon the molecules of **15** on the NMR timescale. On the other hand, the unsolvated compound **16** displays remarkable dynamic behaviour. As ^{1}H-EXSY studies have revealed, the Li atom appears to "rotate" around the N_3Sn unit, generating an effective threefold molecular symmetry at the fast exchange limit.[22,23] This intramolecular motion is reminiscent of the dynamic behaviour reported by Veith and co-workers for a tetraamidoindate, although it appears to take place much more rapidly in the latter case.[24]

The matter of which of the structural alternatives discussed above is observed in a given case was found to be largely unpredictable. It was therefore thought that the design of an amido tripod containing a specific binding site for the metal cation in the ligand periphery would yield "ion pairs" of predefined arrangement.

In an extension of our concept of the "active ligand periphery" in polydentate amides[25,26] containing additional donor functions for cation binding, we synthesised a tripod with peripheral 2-anisyl groups. The synthesis of the lithium stannate cage containing this ligand system (Scheme 5) did indeed give the expected aggregation pattern with intramolecular Li^+ solvation by two of the three *ortho*-anisyl groups, as confirmed by X-ray crystallography (Figure 8).[27]



Scheme 5. Synthesis of a triamidostannate possessing secondary donor function for intramolecular cation solvation

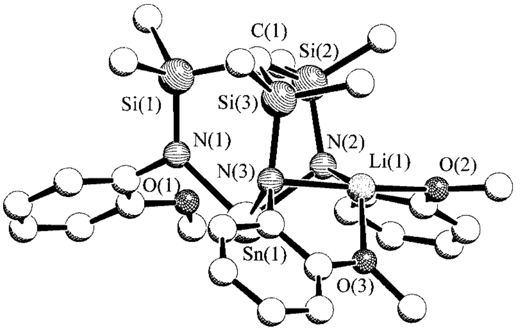


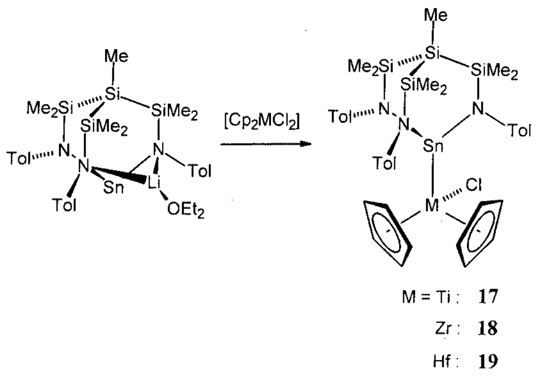
Figure 8. Intramolecular Li^+ solvation in the *ortho*-anisyl-substituted stannate $[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3SnLi]$

Triamidometallates Coordinated to Early Transition Metals

On going from the late to the early transition metals, the polarity and, concomitantly, the reactivity of the metal−metal bonds increase significantly.[28] Whereas group 4 M−Si compounds have found wide-ranging applications, such as in a variety of metal-mediated catalytic processes and in semiconductor growth,[29] their tin analogues remain extremely rare and thus poorly studied, despite numerous efforts to develop their chemistry.[30] A principal problem appears to be that many of the synthetic strategies employed for M−Sn bond formation do not work well when M is titanium, zirconium or hafnium.

A fundamental difficulty in group 4/group 14 metal−metal bond formation is the existence of energetically low-lying electron-transfer reaction pathways from the group 14 metal to the early transition metal. This problem is not unlike the situation in early−late heterodinuclear transition metal complexes, referred to above, in which metals from the two ends of the d-block are directly bonded to each other.[16]

With the aim of obtaining heterodinuclear complexes of greater stability than previously observed, the triamidostannate complex $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3\text{-}SnLi(OEt_2)]$ was treated with the metallocene dichlorides $[Cp_2MCl_2]$ of all three titanium group metals.[31] Nucleophilic substitution of one of the chloro ligands in the metallocene dichlorides occurred cleanly in all three cases, yielding the corresponding dinuclear complexes as thermally stable solids (Scheme 6).



Scheme 6. Synthesis of the stable group 4/group 14 heterodimetallic complexes **17−19**

Single-crystal X-ray structure analyses of both **18** and **19** confirmed the molecular structures and established the presence of the group 4/group 14 metal−metal bonds (Figure 9).[31] The Zr−Sn bond length in compound **18** is, at 3.0231(2) Å, significantly longer than the sum of the covalent radii of the two metals as given by Pauling[32] (ca. 2.85 Å). However, it is in the same range as the Zr−Sn distances in $[Zr(CO)_5(SnMe_3)_2]^{2-}$ [3.011(3) Å] and $[Zr(CO)_4(dppe)SnMe_3]^-$ [3.061(2) Å] reported by Ellis and co-workers.[33] This observation is remarkable, since the latter compounds are low oxidation state zirconium complexes with high coordination numbers, and so should be expected to possess Zr−Sn bonds longer than those in **18**. It is quite likely that the length of the metal−metal bond in **18** is largely dictated by the repulsion of the ligand spheres of the two metal atoms.

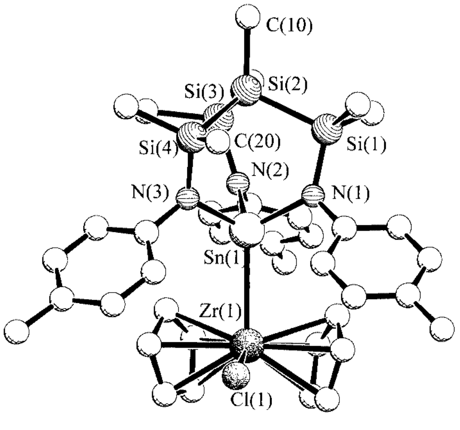


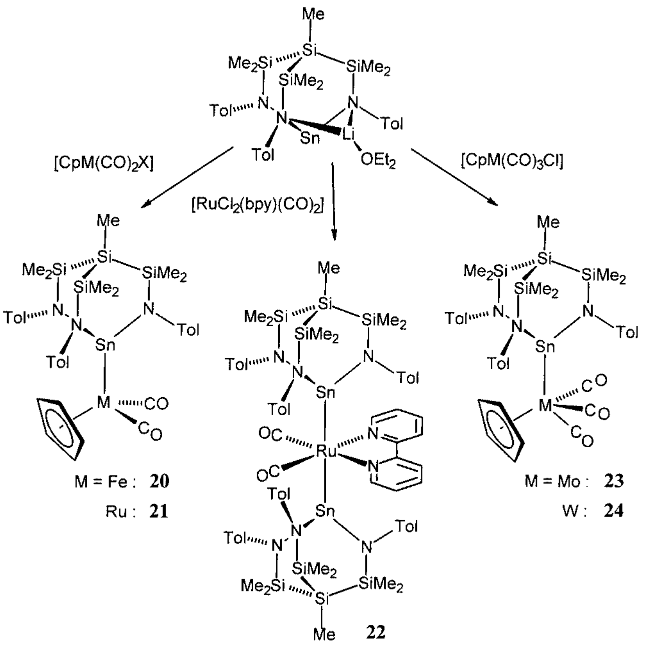
Figure 9. Molecular structure of the Zr−Sn heterodimetallic complex $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn{-}Zr(Cp)_2Cl]$ (**18**)

On comparing the molecular structure of complex **19** with that of **18**, it was interesting to note that all bonds to hafnium in **19** are significantly shorter than those to the zirconium centre in **18**. In particular, the Hf−Sn distance of 2.9956(3) Å is shortened by almost 0.03 Å relative to the analogous Zr−Sn bond and is very similar to the Hf−Sn bond lengths determined in $[(\eta^6\text{-}C_6H_5CH_3)_2Hf(SnMe_3)_2]$, reported by Green and co-workers.[34] There had been one previous study in which two analogous Zr−Sn and Hf−Sn complexes were structurally characterized by X-ray diffraction, and this revealed a very similar relationship between the metal−metal bond lengths in both complexes.[35]

In spite of the long Zr−Sn and Hf−Sn bonds, both compounds **18** and **19** are remarkably stable. No appreciable decomposition was observed when they were heated at reflux in toluene, and as solids they may be briefly handled in air, very probably due to the effective shielding of the highly polar metal−metal bond by the surrounding bulky ligand periphery.

Triamidometallates Coordinated to Late Transition Metals

The triamidostannate cages discussed in this review may readily be coupled with carbonyl halide complexes of the late transition elements, by the same approach as described for the group 4 derivatives in the previous section.[36] Several examples of such late transition metal tin complexes, all obtained by salt metathesis of a stannate with the respective chloro or bromo complexes, are summarized in Scheme 7.[37]



Scheme 7. Coordination of a tripodal triamidostannate to late transition metal complex fragments

In the molecular structure of **22**, depicted in Figure 10, the two $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn]^-$ ligands are bonded to the Ru centre in a nearly linear fashion [Sn(1)−Ru−Sn(2) 174.26(2)°] and are staggered with respect to their tolyl groups. The Ru−Sn bond lengths of 2.7085(5) and 2.7324(5) Å are slightly longer than the typical value for Ru−Sn bonds (2.55−2.69 Å)

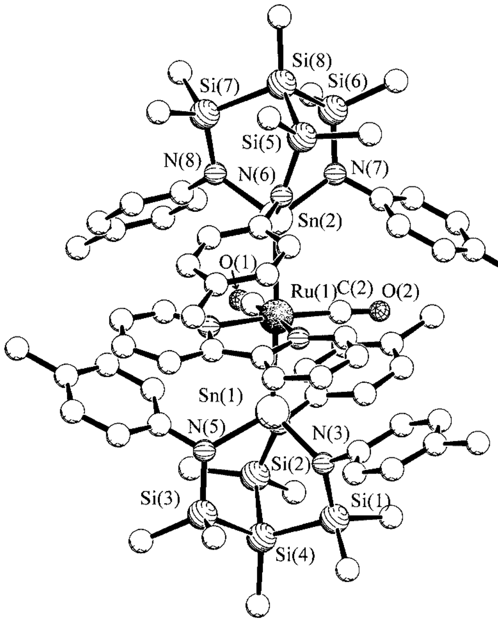


Figure 10. Molecular structure of the Sn−Ru−Sn complex **22**

Although the anionic complex $[(Ph_3Sn)Ni(CO)_3]^-$ was first reported by Kruck et al. in 1969, there had been no report of a crystal structure of an $[(R_3Sn)Ni(CO)_3]^-$ anion in the literature. Treatment of the chiral lithium stannate $[HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3Sn{-}Li(THF)]$ (**15**) with $[Ni(CO)_4]$ cleanly gave the Ni−Sn complex $[Li(THF)_4][HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3Sn{-}Ni(CO)_3]$ (**25**).[22] Crystals of **25** were found to be extremely air- and moisture-sensitive, and therefore had to be selected and mounted at ca. −80 °C. In the [2.2.2]bicyclooctane-derived cage, one of the bridgehead positions is occupied by the $Sn{-}Ni(CO)_3$ fragment (Figure 11).

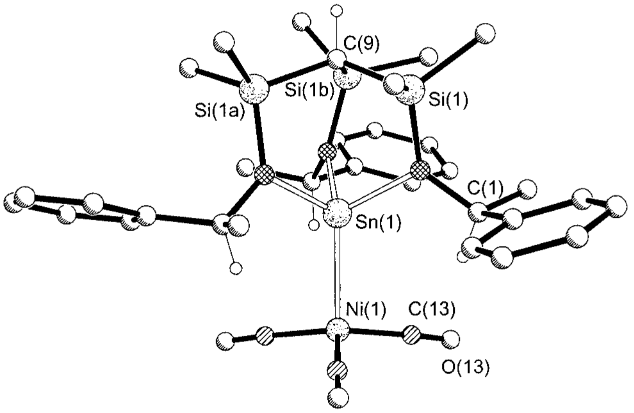


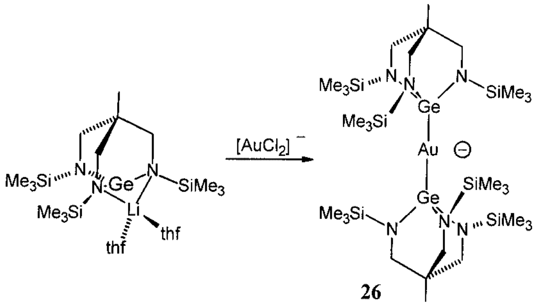
Figure 11. Molecular structure of the Ni−Sn complex $[HC\{SiMe_2N[(S)\text{-1-phenylethyl}]\}_3Sn{-}Ni(CO)_3]$ (**25**), containing a C_3-chiral triamidostannate

The Sn(1)−Ni(1) vector is aligned along the threefold crystallographic axis, imposing exact C_3 symmetry upon the anion. The Sn−Ni bond length of 2.492(2) Å is unexceptional; however, we note that the coordination of the Lewis acidic $Ni(CO)_3$ fragment to the Lewis basic stannate effects a significant shortening of the Sn−N distances [Sn(1)−N(1) 2.086(6) Å] in comparison to those in the lithium stannate **15** [average Sn−N 2.174(6) Å]. The stannate ligand is readily displaced from the nickel by better donors such as phosphanes and isocyanides.[22]

Triamidometallates Coordinated to the Coinage Metals: Copper, Silver and Gold(I, II and III) Complexes

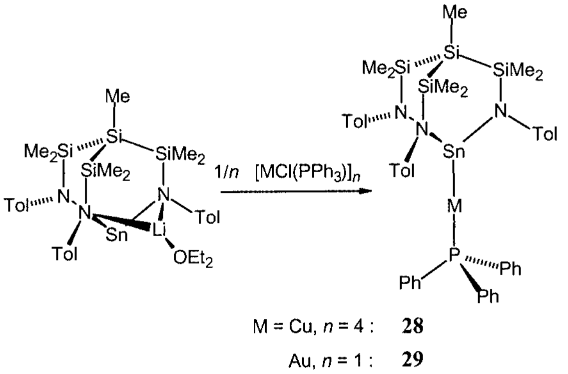
In contrast to the extensive investigations into the chemistry of organometallic complexes of the coinage metals, there have, until recently, been comparatively few compounds containing direct metal−metal bonds between copper, silver or gold and the heavier group 14 elements.[38]

We were able to provide the first crystallographically characterized example of a digermanylaurate (**26**) by treatment of the triamidogermanate(II) $[MeC(CH_2NSiMe_3)_3Ge{-}Li(THF)_2]$ with $[Ph_4P][AuBr_2]$, the corresponding Sn−Au−Sn analogue also being accessible by the same route (Scheme 8).[39]



Scheme 8. Synthesis of the first digermanylaurate **26**

Treatment of the stannate $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3SnLi(OEt_2)]$ (**27**) with 0.25 mol-equiv. of $[CuCl(PPh_3)]_4$ or 1 equiv. of $[AuCl(PPh_3)]$ in toluene at room temperature gave the corresponding Sn−Cu and Sn−Au complexes $[MeSi\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn{-}Cu\text{-}$



Scheme 9. Synthesis of the coinage metal/tin compounds **28** and **29**

(PPh$_3$)] (**28**)[37] and [MeSi{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$-Sn−Au(PPh$_3$)] (**29**) (Scheme 9).[40] The formation of Sn−Cu and Sn−Au bonds in these complexes is supported by the observation of $^{117/119}$Sn satellites in their ^{31}P NMR spectra. Neither compound apparently undergoes detectable redistribution reactions in solution.

The crystal structure of **29** confirms the conclusions drawn from the spectroscopic data. In its molecular structure (Figure 12), the triamidostannate cage is directly bonded to the Ph$_3$PAu unit [*d*(Au−Sn) = 2.5651(13) Å], the gold atom adopting an essentially linear geometry [<(Sn−Au−P(1) = 179.9(1)°], as expected for monovalent gold. This Sn−Au distance is slightly shorter than that found for [Au$_8$(PPh$_3$)$_7$(SnCl$_3$)][SnCl$_6$] [2.625(3) Å],[41] and considerably shorter than those in the tricoordinate Au^I complex [(PMe$_2$Ph)$_2$AuSnCl$_3$] [2.881(1) Å][42] and in the polynuclear compound [Au$_4$(PPh$_3$)$_4$(μ$_2$-SnCl$_3$)$_2$] [2.8150(7), 2.9725(8) Å], for which a weak Sn−Au interaction was proposed.[43]

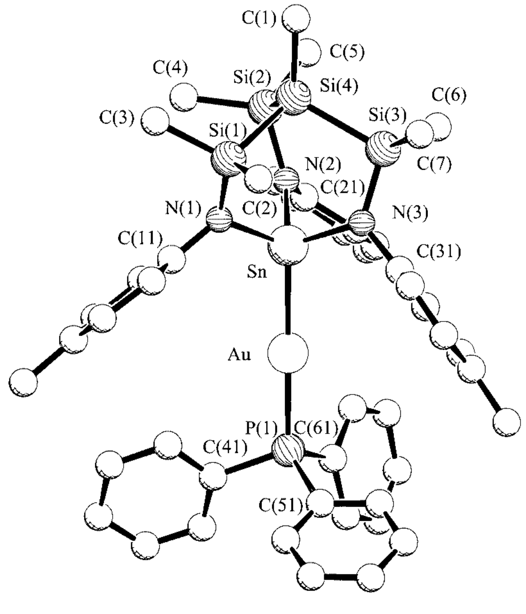


Figure 12. Molecular structure of [MeSi{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$Sn−Au(PPh$_3$)] (**29**)

The stannate **27** reacts with various other gold halide complexes by salt metathesis and formation of the metal−metal bond to afford the respective tin−gold heteronuclear compounds. By this approach, gold(I−III) complexes **30**−**34** have been obtained upon treatment of the stannate with [PPN][AuCl$_2$], [PPN][AuCl(R)] (R = C$_6$F$_5$, mesityl), [Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$Cl$_2$] and [PPN]-[AuCl(C$_6$F$_5$)$_3$], respectively (Scheme 10).[40]

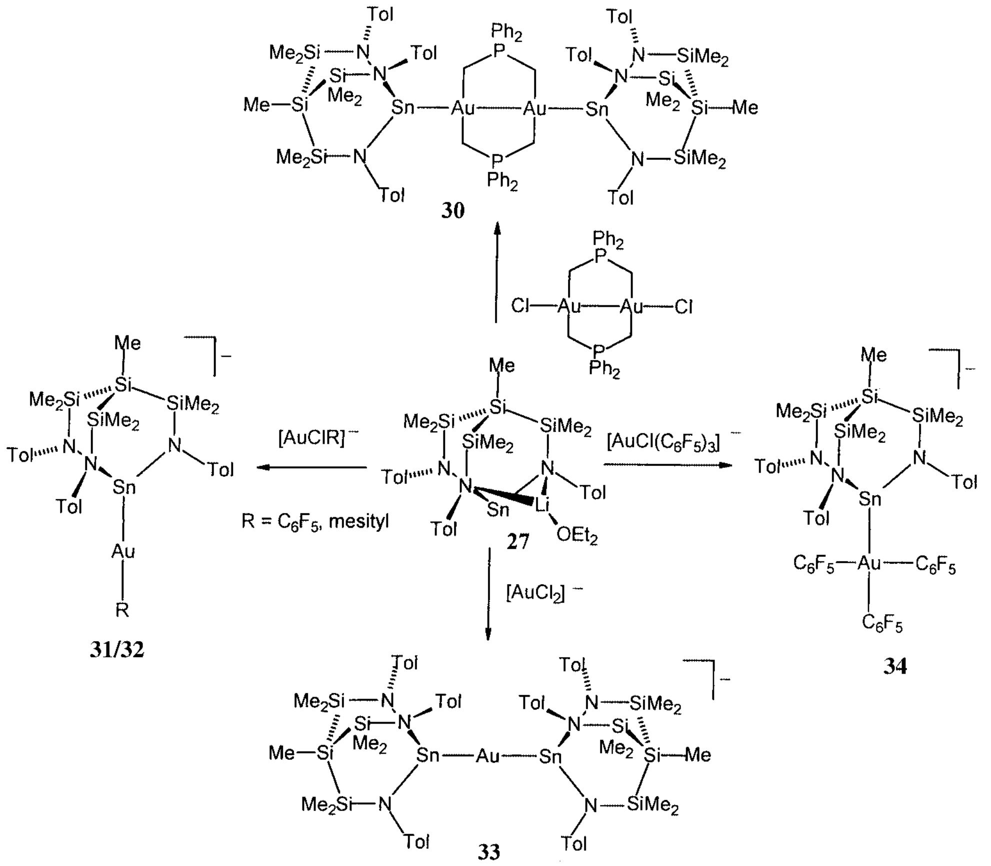
An X-ray diffraction study of the first example of an Sn−Au^{II} complex **30** established the details of its molecular structure (Figure 13). The Sn−Au bond length is 2.6804(13) Å, and thus significantly longer than the Sn−Au distance in the gold(I) derivative [MeSi{Me$_2$SiN(*p*Tol)}$_3$-SnAu(PPh$_3$)] (**29**) discussed above [2.5651(13) Å]. This may be a consequence of the steric repulsion between the periphery of the tripodal amido ligand and the bis(ylide) ligands coordinated to the Au$_2$ unit. The coordination geometry of the gold(II) centres is square-planar, as usually exhibited in gold(II) derivatives with gold−gold bonds. The Au^{II}−Au^{II} distance is 2.7492(13) Å, one of the longest found in these type of gold(II) complexes, the only species with a longer Au−Au bond being [{(C$_6$F$_5$)Au-(CH$_2$PPh$_2$CH$_2$)$_2$Au}Au(C$_6$F$_5$)$_2$][Au(C$_6$F$_5$)$_4$] [2.755(1) Å].[44]

Ag−Sn heterobimetallic compounds are particularly rare, the only known molecular species containing an Ag−Sn bond prior to our studies being [(Ph$_3$P)$_3$AgSnCl$_3$].[44] While this compound has been the object of several spectroscopic studies, there was no direct structural proof for an Sn−Ag bond. Since stannous chloride finds applications in photography as a reduction sensitizer for silver halide emulsions,[46] a more detailed investigation of such Ag^{I}Sn^{II} systems was of general interest.

Upon treatment of **27** with 0.25 mol-equiv. of [(Ph$_3$P)AgCl]$_4$, the two Ag−Sn-bonded phosphane-containing products together with [MeSi{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$Sn−Ag(PPh$_3$)] (**35**) and [MeSi{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$Sn−Ag(PPh$_3$)$_2$] (**36**) were detected in solution, the latter being directly accessible by treatment of the stannate with [Ag(PPh$_3$)$_2$][CF$_3$SO$_3$] (Scheme 11). The phosphane-free component **37** in this equilibrium mixture could be isolated by fractional crystallization. While the analytical data were consistent with a formulation of **37** as [MeSi{SiMe$_2$N(*p*Tol)}$_3$Sn−Ag]$_n$, a single-crystal X-ray structure analysis established a dimeric structure corresponding to [MeSi{SiMe$_2$N(*p*Tol)}$_3$Sn−Ag]$_2$ (Figure 14).[47]

The molecular structure of **37** is based on a centrosymmetric dimeric molecular unit featuring two Sn atoms, each coordinated by a tripod-triamido ligand. Each Sn atom links to an Ag atom through an Sn−Ag bond [*d*(Sn−Ag) = 2.6567(7) Å]. The two Ag centres in the complex are in close proximity; the *d*(Ag−Ag′) distance [= 2.6544(11) Å] is among the shortest ever observed in Ag^I aggregates and may indicate a significant d^{10}−d^{10} attraction. In **37**, the ligand periphery plays an "active" role and facilitates the dimerization of the silver stannate units. These monomer units are linked by η^2-coordination of one tolyl group of each tripodal amido ligand to the silver atom of the opposite unit [*d*(Ag−C25′) = 2.604(5); *d*(Ag−C26′) = 2.374(4) Å], the asymmetry of the η^2-coordination in the complex being typical of arene−Ag^I interactions.[48]

The presence of a ligand redistribution equilibrium of the Ag−Sn complexes is a manifestation of the propensity of Ag^I species to attain coordination numbers higher than two. The displacement of the phosphane ligand may additionally be favoured by the possibility of "arene solvation" of the Ag centres. This study provided the first direct structural evidence for an Ag−Sn bond. More recently, however, Lappert and co-workers have reported another structurally characterized Ag−Sn heterodimetallic complex.[49]



Scheme 10. Synthesis of $Au^{I}-Sn$, $Au^{II}-Sn$ and $Au^{III}-Sn$ complexes

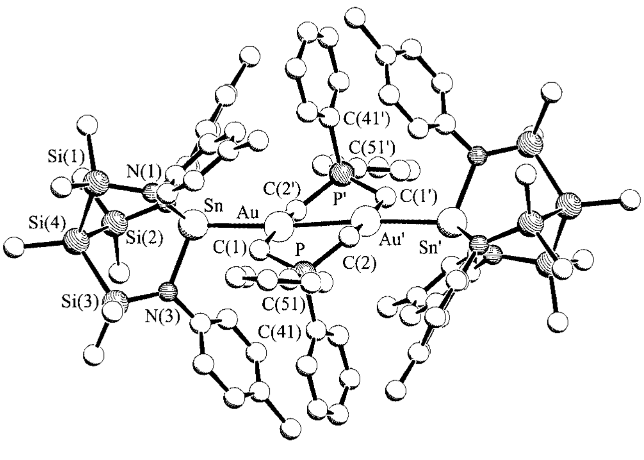
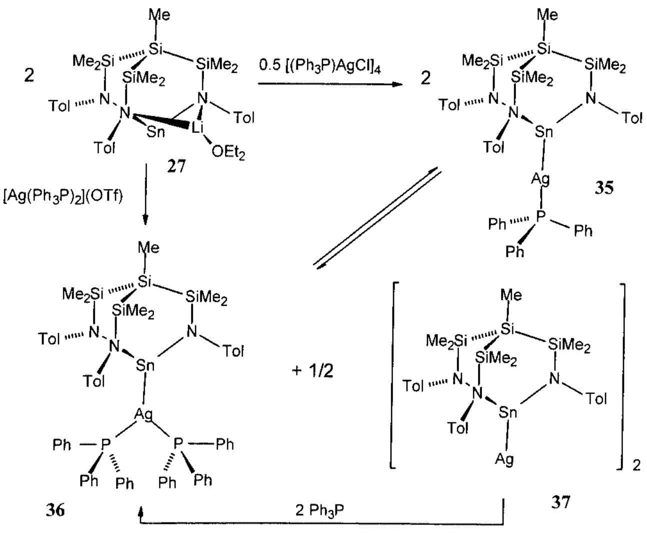


Figure 13. Molecular structure of the $Sn-Au^{II}-Au^{II}-Sn$ complex **30**



Scheme 11. Ag−Sn complexes **35−37**, which are in equilibrium in solution, upon treatment of the lithium stannate **27** with $[AgCl(PPh_3)]_4$

Group 12 Metal/Tin Complexes

Complexes containing bonds between group 12 metals and a group 14 element are versatile reagents in synthetic chemistry. The most prominent examples are cyclopropanation reactions with (α-halomethyl)mercury compounds,[50] the reductive replacement of mercury by hydrogen, the use of $Hg(SiMe_3)_2$ as a silylating reagent[51] and the photolytic cleavage of $Hg(SiMe_3)_2$ to yield silyl radicals.[52] Although a few examples of structurally characterized complexes with the lighter group 14 metals (Si, Ge)[53] have been reported, and compounds such as $R_3Sn-Hg-SnR_3$ have been spectroscopically studied in detail,[54] there was, at the time we began our studies, no direct structural characterization of

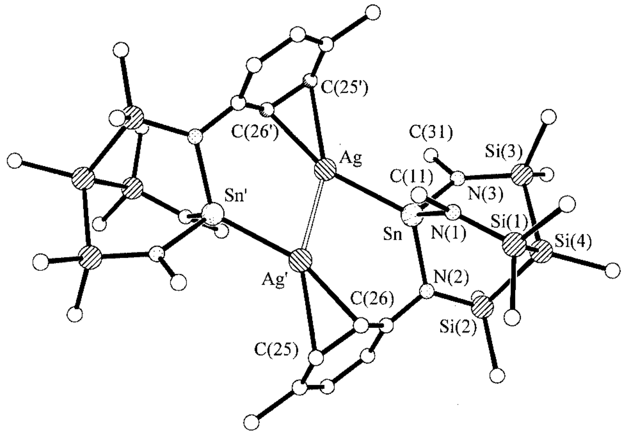
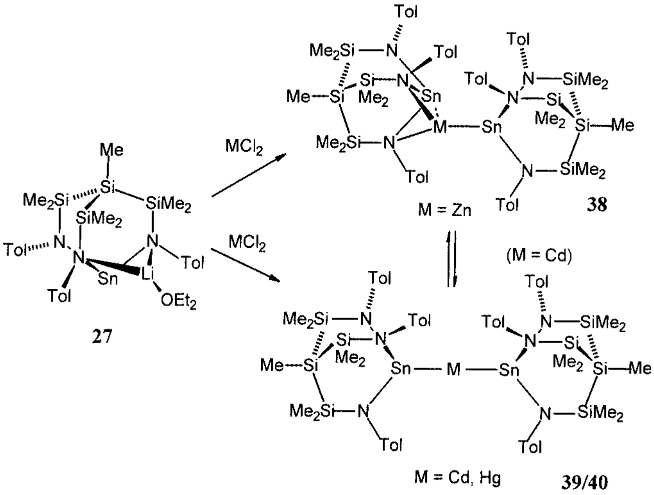


Figure 14. Molecular structure of the first crystallographically characterized Ag−Sn complex; the two molecular units are linked by attractive Ag−arene and Ag−Ag interactions; the peripheral tolyl groups not coordinated to Ag are omitted in this representation for clarity

either Sn−Hg or Sn−Cd bonds and only a single example of a crystallographically authenticated Sn−Zn complex[55] to be found in the literature.

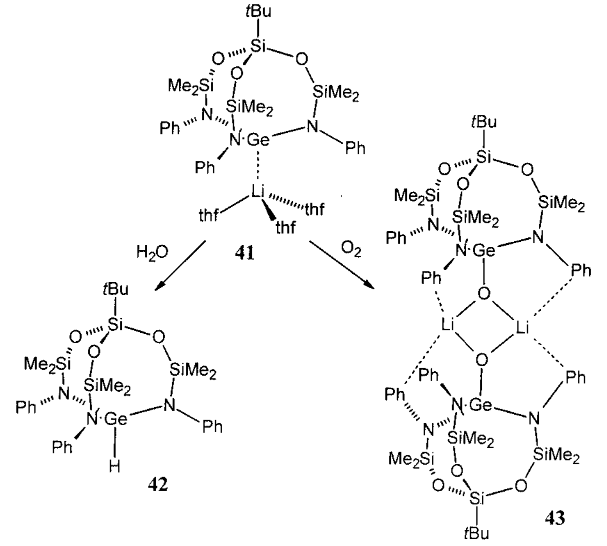
Treatment of the lithium stannate **27** with MCl_2 (M = Zn, Cd, Hg) cleanly gave the corresponding Sn−M−Sn complexes **38**−**40** (Scheme 12).[56] Whereas the linear Sn−Hg−Sn complex is stable in solution, the cadmium compound **39** − while also linear in the crystal − is in equilibrium with a second, less symmetrical isomer, as became evident from NMR studies carried out in solution. This second structural arrangement is the most stable form of the Sn−Zn−Sn complex **38** and is also found in its crystal structure.[56] Here the tendency of the "dication" Zn^{2+} to adopt coordination numbers greater than two and ligands containing hard donor atoms becomes readily apparent.



Scheme 12

Beyond the Rigid [2.2.2]Bicyclooctane Cage

Recent work from Veith's group indicates that the principles outlined in this overview might possibly be extendable to systems with less rigid structures. Those workers synthesized the tripodal amido ligand $[t\mathrm{BuSi(OSiMe_2NPh)_3}]^{3-}$,[57] which was coordinated to divalent germanium, to give a lithium triamidogermanate with a direct Ge−Li bond $[t\mathrm{BuSi(OSiMe_2NPh)_3Ge{-}Li(THF)_3}]$ (**41**). This compound was in turn hydrolysed to give the corresponding Ge−H germane **42** and oxidized to yield the lithium oxogermanate(IV) **43** (Scheme 13).[58]



Scheme 13

The different orientation of the N-donor functions imposed by the expanded ligand framework allows for structural motifs somewhat different to those that we found for the systems discussed above. It will be interesting to learn more about the "ligand" properties of these systems.

Conclusions and Outlook

The combination of thermodynamic stabilization of the triamidometallates by their integration into a rigid molecular cage structure, along with the well-defined orientation and high variability of the peripheral N-substituents, has established tripodal triamidometallates as a versatile new class of ligands in the coordination chemistry of the transition metals. The electronegative N-substituents at the divalent metal atoms render them less oxidizable than would be expected for alkyl- or aryl-substituted derivatives.

The first results of our attempts to stabilize low-coordinate late transition metal complexes with catalytically relevant metals such as rhodium or palladium suggests that the monoanionic group 14 metallates, apart from being objects of study in their own right, may find applications in the development of novel homogeneous catalysts.

Acknowledgments

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